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Scanning Electron Microscopy of the Effects of Moisture and Elevated Temperature on the Fibre/Matrix Bond in CFRP

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SCANNING ELECTRON MICROSCOPY OF THE EFFECTS OF MOISTURE AND ELEVATED TEMPERATURE ON THE FIBRE/MATRIX BOND IN CFRP

by

G.D. Howard

SUMMARY

The fibre/matrix interface is of paramount importance since it provides the bond between the load-bearing fibres and the resin matrix. There is evidence that degradation of the fibre/matrix interface occurs, not only as a result of the thermal spiking of environmentally conditioned CF/epoxy resin systems but also solely as a result of their prolonged exposure to high humidity environments. This Memorandum describes a preliminary study and further work in this area would be beneficial.

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1 INTRODUCTION

The engineering properties of carbon fibre reinforced plastics (CFRPs) make them attractive materials with potential applications in many demanding markets. Because of their low density, CFRPs have high specific strength and stiffness thus offering substantial savings in weight. For these reasons, composites such as carbon fibre reinforced epoxy resins are increasingly being used in aircraft primary and secondary structures.

Unlike metals however, epoxy resins are moisture-sensitive and absorbed moisture can affect the properties of the composite as a whole. Today's military aircraft can also experience rapid high temperature excursions called 'thermal spikes' caused by air friction during supersonic flight or ground-reflected efflux from the engines of VTOL aircraft.

Recent work[1&2] at RAE described in the text, suggests that not only is the resin matrix degraded by absorbed moisture, but also that the fibre/resin bond is itself degraded. This Memorandum describes an investigation using scanning electron microscopy (SEM) techniques to examine the fibre/resin interface for signs of degradation due to prolonged exposure to high humidity and thermal spiking.

2 BACKGROUND INFORMATION

The carbon fibres available today were developed first at RAE Farnborough in the 1960s. They are very stiff, strong and lightweight and do not readily deform under changes in temperature. Carbon fibres are elastic to failure at normal temperatures and this total lack of plasticity means that they do not creep and they are not susceptible to fatigue. To be of practical use, however, the fibres have to be made into a composite material with an appropriate matrix. It can therefore be said that a fibre composite consists of three parts namely:

The fibres - which are load bearing and provide stiffness along the fibre direction.

The matrix - which carries shear loads, transfers load between the fibres and supports the fibres when in compression, and:

The fibre/resin bond - which is of paramount importance since many of the mechanical properties of CFRP are markedly affected by the strength of the bond between the resin matrix and the fibre surface.

If the bond is too weak the loads will not be fully transferred from the matrix to the fibres and the full potential of the material will not be realised. However if the bond is too strong the composite is brittle and properties such as impact strength and shear strength will be unacceptably poor.

To date, thermosetting resins constitute the majority of resins used in organic matrix fibre composites since at the time that carbon fibres in their present form were developed such resins were already being used in glass reinforced plastics (GRP). Of the thermosets the most commonly used in aircraft structural parts are the epoxides. Epoxy resins have a higher glass transition temperature (T_g) than many thermoplastics. They also possess comparatively good mechanical properties, are relatively easy to fabricate and they adhere well to carbon fibres.

It is generally accepted that epoxy resins absorb moisture (water) from the air and that, depending on the type of reinforcement employed[3], this affects the mechanical performance of the composite. Because carbon is inert the fibres in CF/epoxy resin systems are unaffected but the properties of the matrix are altered by environmental exposure. Temperature is a key parameter since the outer skins of supersonic aircraft can experience temperatures ranging from -60°C to +132°C. Such temperature changes can occur very rapidly and give rise to 'thermal spikes'. It has been shown[4] that these spikes can cause damage to CFRP if absorbed moisture is present in the material. Recent work shows that the fibre/resin bond is also degraded by exposure to moisture and elevated temperature. The purpose of this investigation was to ascertain whether the fibre/resin interface is attacked by a combination of moisture and elevated temperature or whether damage is caused merely by prolonged exposure to high humidity environments.

3 MOISTURE ABSORPTION BEHAVIOUR

The process by which CFRP structures readily absorb moisture from the air when exposed to a humid environment is well documented. Initial moisture absorption usually obeys Fick's law of diffusion. Shen and Springer[5] showed that the diffusion coefficient can be expressed in terms of the percentage moisture by weight and can be obtained from the slope of the initial linear portion of a graph of moisture uptake against root time. The amount of moisture absorbed generally depends only on the relative humidity (RH) of the environment and is usually independent of temperature providing the glass transition temperature of the resin (T_g) is not exceeded. Fig 1 shows typical moisture absorption curves at two temperatures for a carbon fibre reinforced plastic which was initially dry. The moisture content was determined by weighing and this was plotted against root time. Absorption of moisture causes the resin to swell. This relives residual stresses which are present in a dry laminate due to the different thermal contractions of the fibres and resin matrix on cooling from the moulding temperature. Absorbed moisture also causes a plasticisation of the resin, (*ie* higher strains are achieved when wet), and reduces the glass transition temperature. The reduction in T_g is approximately linear with moisture uptake and for epoxies, is roughly 20°C for every 1% by weight of moisture absorbed[3,6]. There is evidence that thermal spikes cause irreversible damage if the moisture content has been sufficient to lower the T_g to around the spiking temperature. This damage is made evident when on subsequent exposure to moisture, CFRP which has been spiked shows an increase in moisture uptake and increased swelling.

4 EXPERIMENTAL DETAILS

4.1 Mechanical performance

A great deal of work has been carried out to determine the performance of several CF/resin systems conditioned in various environments and subjected to a range of temperature excursions[1&2]. It was found that spikes to +132°C and 'real-life' spikes, consisting of a combination of -55°C for 30 minutes immediately followed by a spike to +132°C, degraded the mechanical properties. Thermal spiking caused a significant increase in moisture absorption in all the materials looked at but was greatest for the CF/resin system investigated here. In a base climate of 75% RH (Fig 2) the moisture contents of spiked specimens were 50% higher than those of the non-spiked controls. It was also found that the increase was greater for base climates with higher humidities. In a base climate of 90% RH the spiked specimens absorbed 70% more moisture than the controls (Fig 3).

At the end of a 20 week spiking period both spiked and non-spiked specimens were tested. Mechanical performance was assessed using a tension test. Specimens were cut with fibres orientated at +45° and -45° and loaded in tension. The specimens deformed in shear parallel to the fibre directions. A test specimen is shown in Fig 4. The failure stress and the secant modulus at 1% strain (which measures the stiffness) were measured. Fig 5 shows the secant moduli at 1% strain for spiked specimens compared with the plot for non-spiked controls. Despite the fact that the spiked specimens contained 50% more moisture the graph shows no decrease in modulus. A similar result was obtained even for specimens in a base climate of 90% RH. It was stated earlier that absorbed moisture acts as a plasticiser, *ie* it 'softens' the resin, so Fig 5 seems to indicate that the extra moisture present in the spiked specimens had not been absorbed by the resin matrix.

In Fig 6 the failure stresses of the same specimens are shown and in this case the strengths of the spiked specimens are consistently lower than the controls. The extra moisture in the spiked specimens could be present in microcracks in the matrix itself but the visual appearance of tested specimens suggested that the fibre/matrix bond had been degraded and this could cause a drop in tensile strength.

To determine this it was therefore decided that the fibre/resin interface should be looked at in some detail.

4.2 Specimen preparation and microscopy

The investigation was confined to thee specimens, one from each of the following conditions:

(i) as received (virgin) material,

(ii) material conditioned to equilibrium at 60°C 90% RH and,

(iii) material saturated at 60°C 90% RH and real-life spiked (this specimen thus contains 70% more moisture than the previous one).

Those specimens selected for microscopic evaluation were cut at an angle of 45° so that, when viewed, fibre ends could be examined for evidence of fibre/matrix debonding. Each section was then set in a mounting compound of Epikote resin and calcium carbonate filler, and cured in an oven at 45°C overnight.

The specimens were polished on four rotary pregrinders, the coarsest grit being used first and the finest grit last. Since the material is plastic liberal amounts of water were applied. Care was also taken to wash the specimens between stages to ensure that no pieces of grit remained from the previous, coarser grade of paper. Further polishing was carried out on polishing pads using metal polish and finally, 1 micron diamond paste.

After being cleaned in an ultrasonic bath the specimens were examined under an optical microscope for signs of fibre/matrix debonding. It was a matter of some concern when no such damage was observed in either of the environmentally conditioned specimens. This was put down to variations in the material itself since degradation of the fibre/resin interface is evident in other cross-sections taken from the same test specimens. Nonetheless it was decided that the investigation should go ahead since the scanning electron microscope is a much more powerful tool. The specimens, (being plastic and thus non-conducting) were coated with gold palladium and viewed in the SEM with the specimen stage set at an angle of 60° to the horizontal. Each specimen was examined in six separate locations through the thickness, between layers as well as deep within a ply. The outer plies were not examined since any damage viewed at the edges could have been caused during specimen preparation. Also, each specimen was viewed at different magnifications.

5 RESULTS AND DISCUSSION

Fig 7 shows micrographs of virgin material which was included as a reference for comparison with the environmentally conditioned specimens. Figs 8 and 9 show micrographs of non-spiked control and 'real-life' spiked material respectively; both specimens having been saturated at 60°C 90% RH. It is clearly evident that the fibre/matrix interface has been attacked in both specimens. This degradation of the fibre/resin bond would account for the extra moisture absorbed by the spiked specimens and the corresponding drop in tensile strength. Also the stiffness (modulus) of the material would remain unaffected if the extra moisture was present in interfacial cracks and not in the resin itself.

6 CONCLUSIONS

(1) Thermal spiking of carbon fibre reinforced epoxy resins causes degradation of the fibre/matrix bond, which could account for the extra 70% by weight of moisture absorbed with no corresponding drop in modulus.

(2) This investigation also showed, however, that if the relatively humidity of the conditioning environment is high enough, the fibre/matrix interface is subject to attack by absorbed moisture alone.

(3) It is acknowledged that an examination of only one specimen form each of three environments is far from substantial. Clearly, further work on this and other fibre/resin systems is required.

Acknowledgments

The author gratefully acknowledges Dr S.M. Bishop, Materials and Structures Department, whose programmes and findings led to the investigation described in this Memorandum.

M.J. Hiley, Materials and Structures Department is also acknowledged for his help and guidance with the SEM work.

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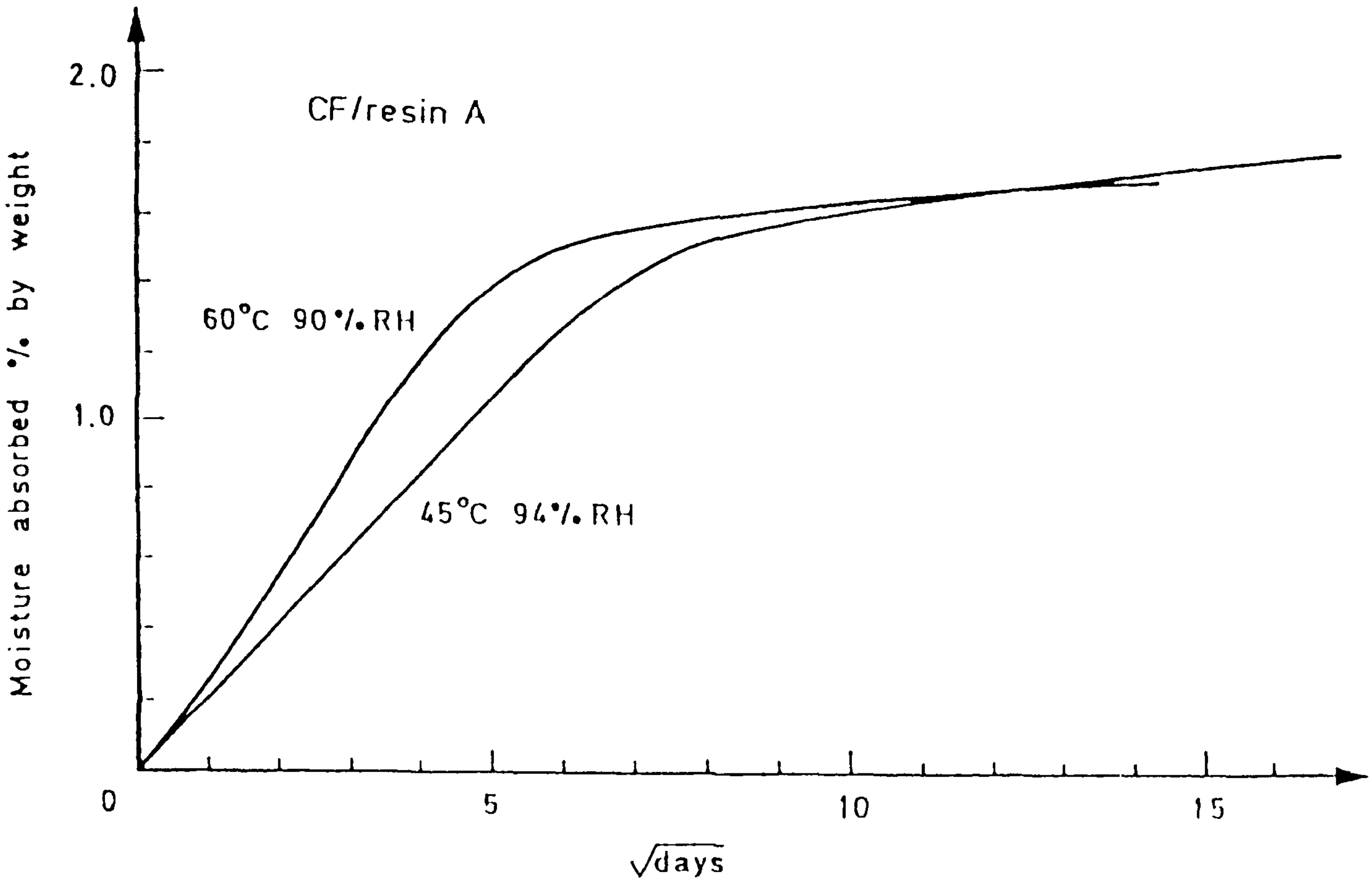


Figure 1 Plots of moisture absorption versus square root time for a carbon fibre reinforced epoxy resin in 45°C 94% RH and 60°C 90% RH environments.

Fig 2

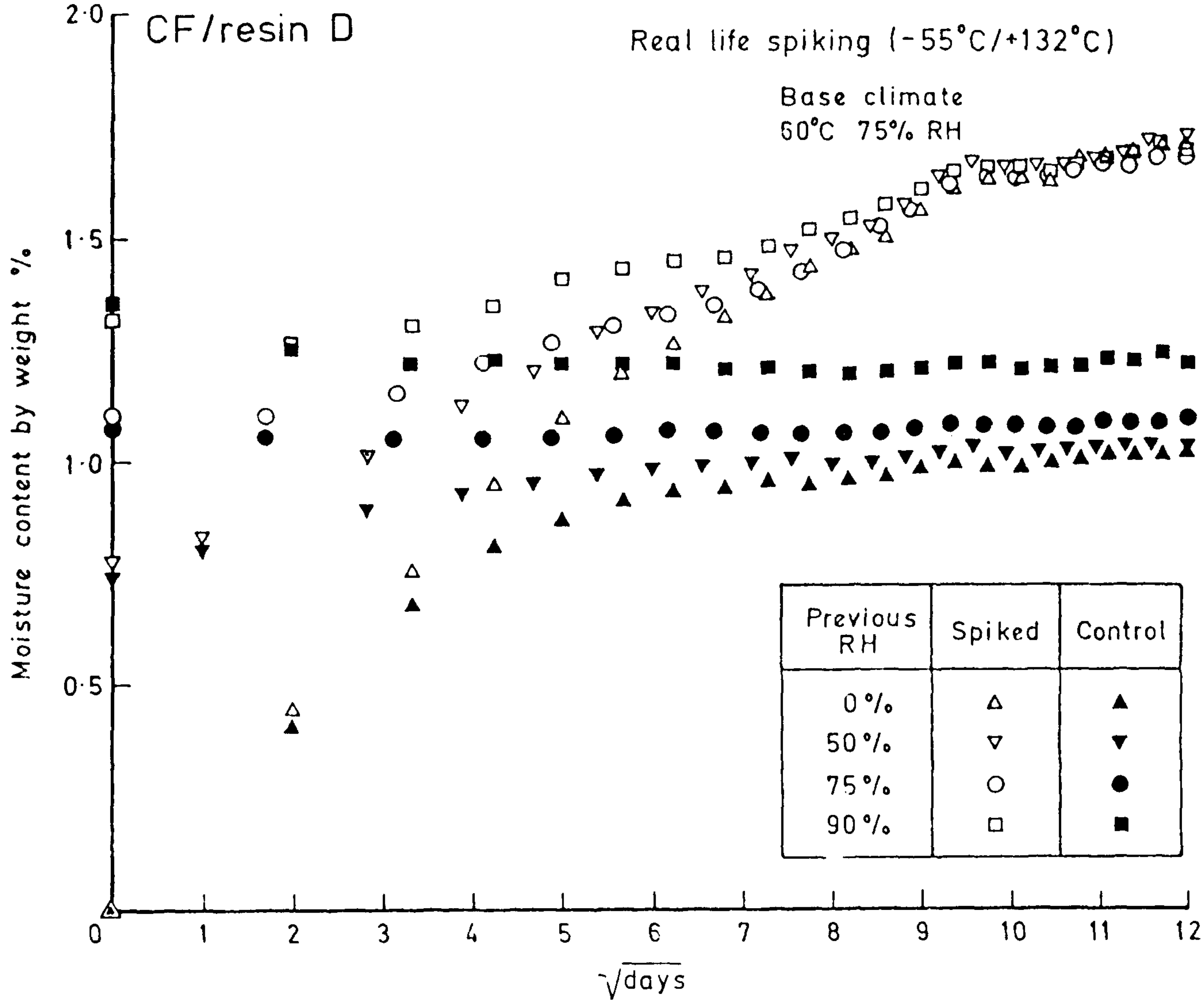


Figure 2 Comparison of moisture absorption of specimens real-life spiked and control specimens of CF/resin D in a base climate of 60°C 75% RH.

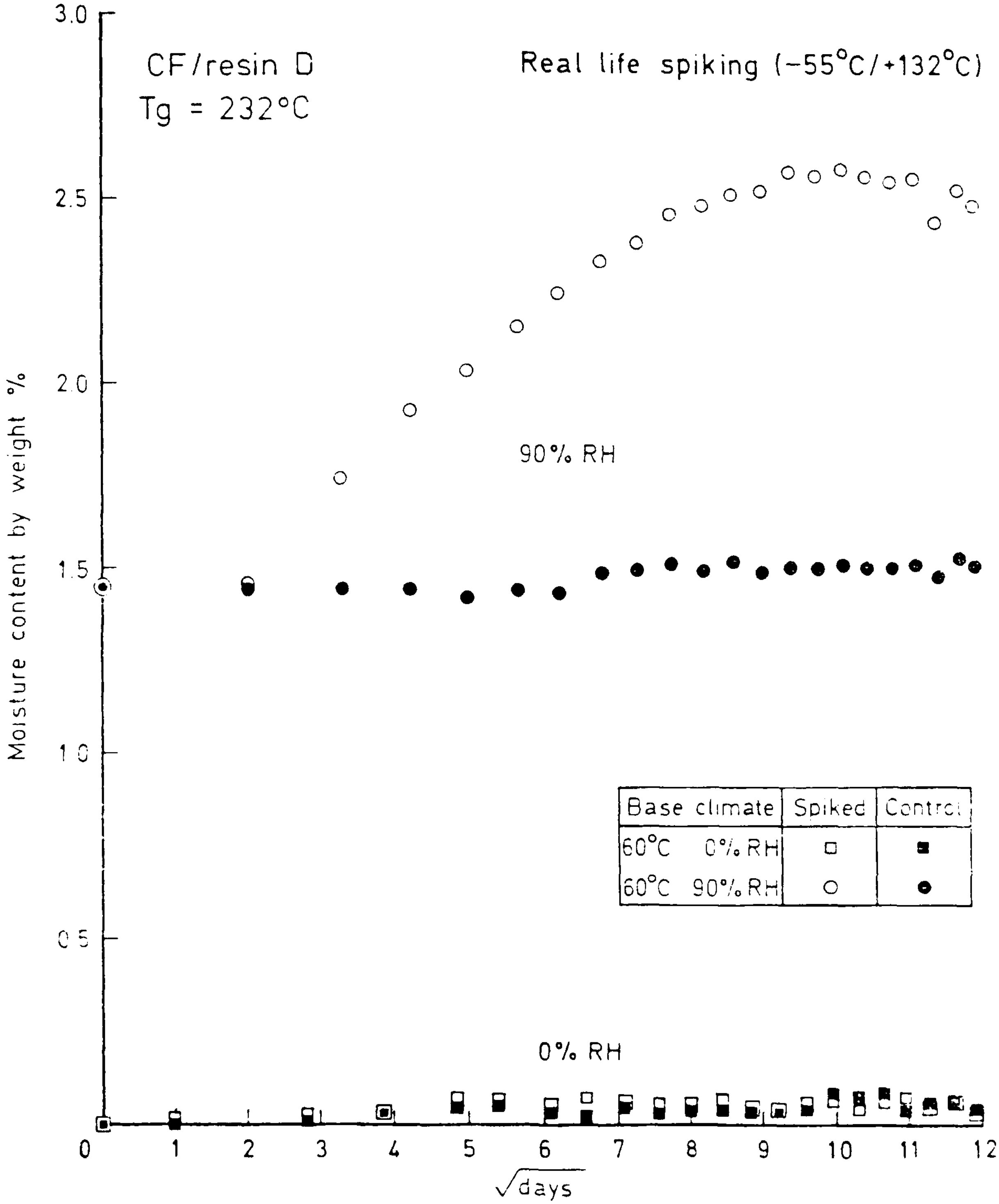


Figure 3 Plot of moisture content against root time for specimens real-life spiked compared with non-spiked controls for two extremes of climate.

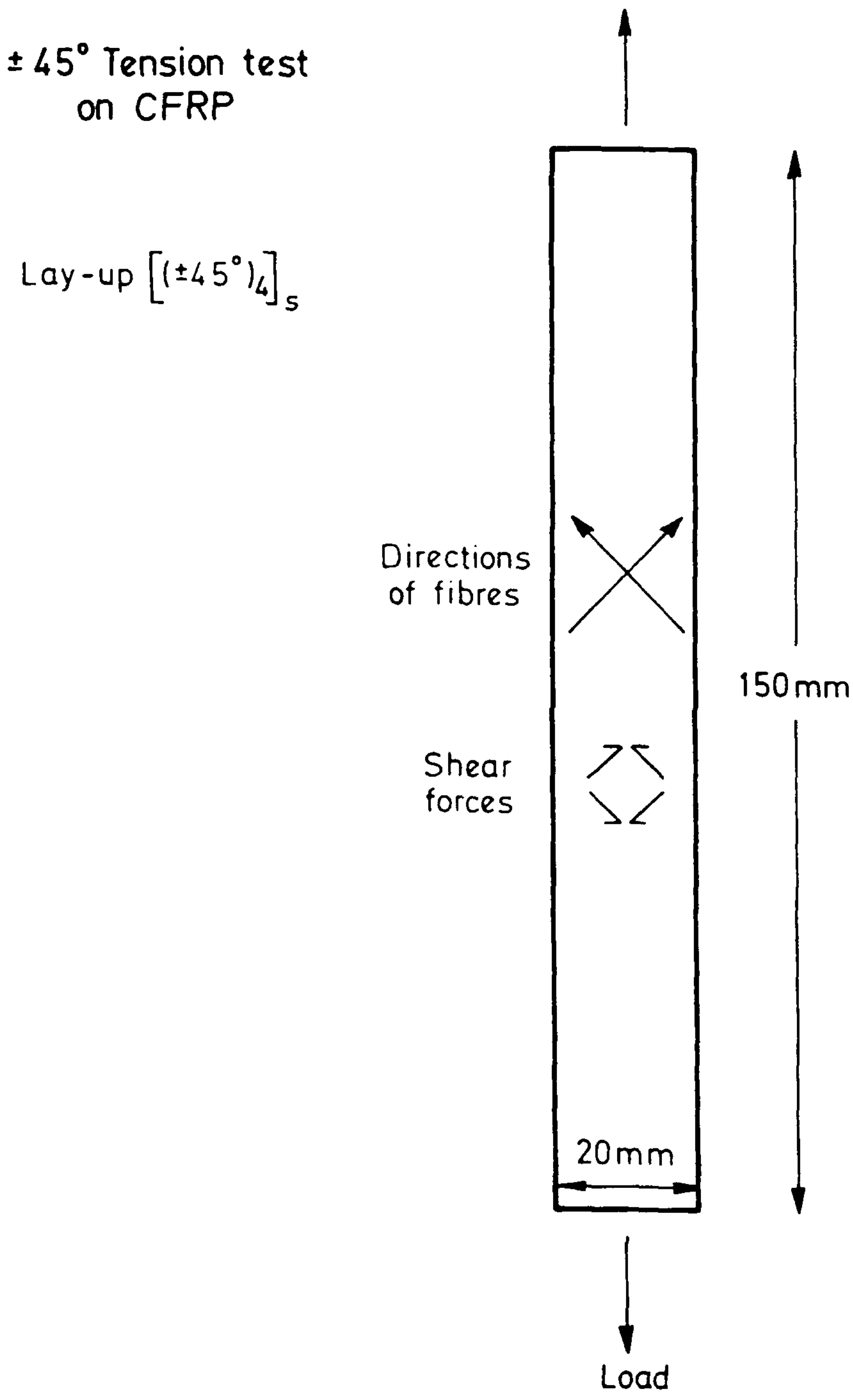


Figure 4   Dimensions and lay-up of test specimens.

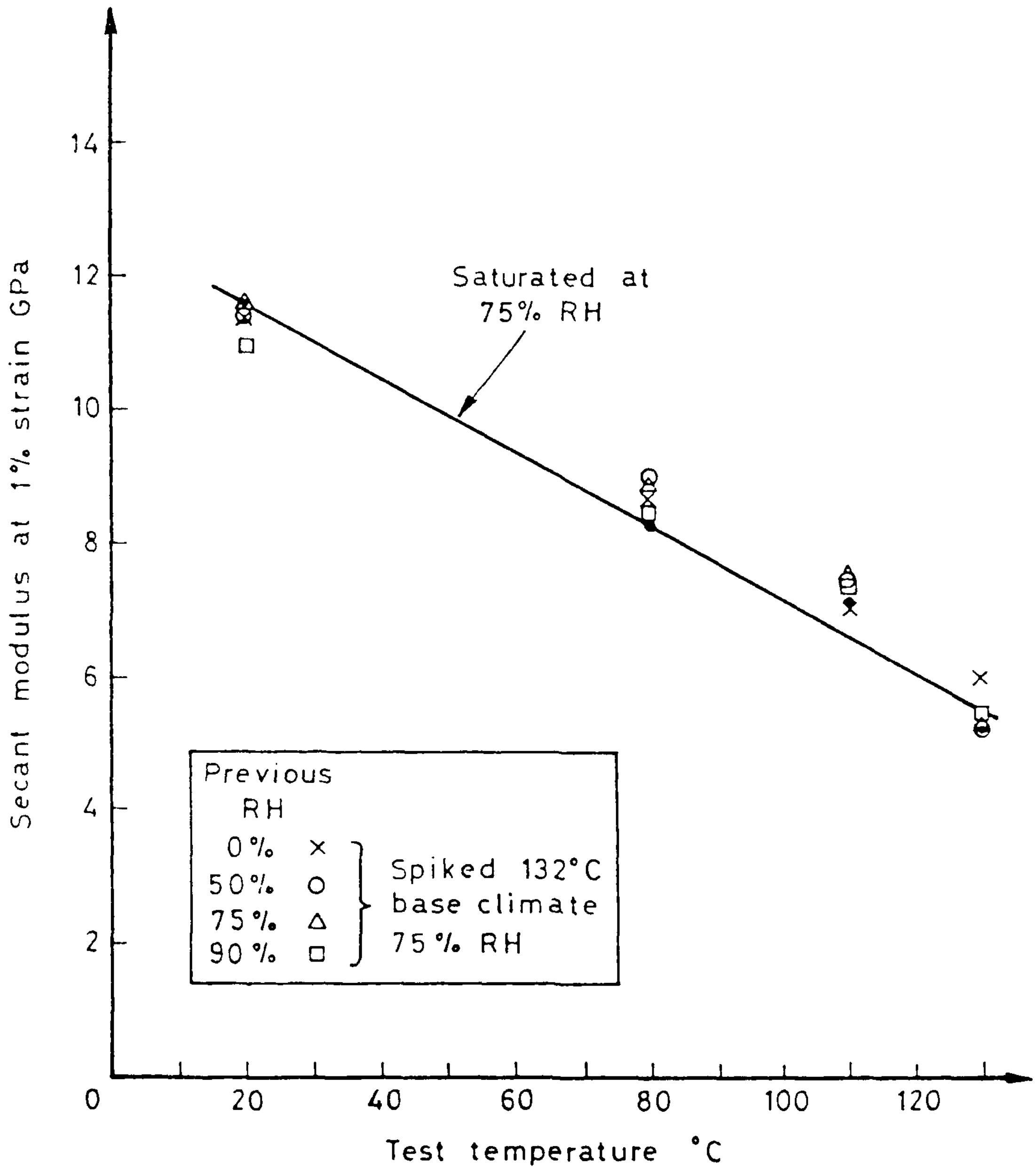


Figure 5 Secant modulus at 1% strain of specimens spiked at +132°C compared with non-spiked controls (straight line) in a base climate of 75% RH.

Fig 6

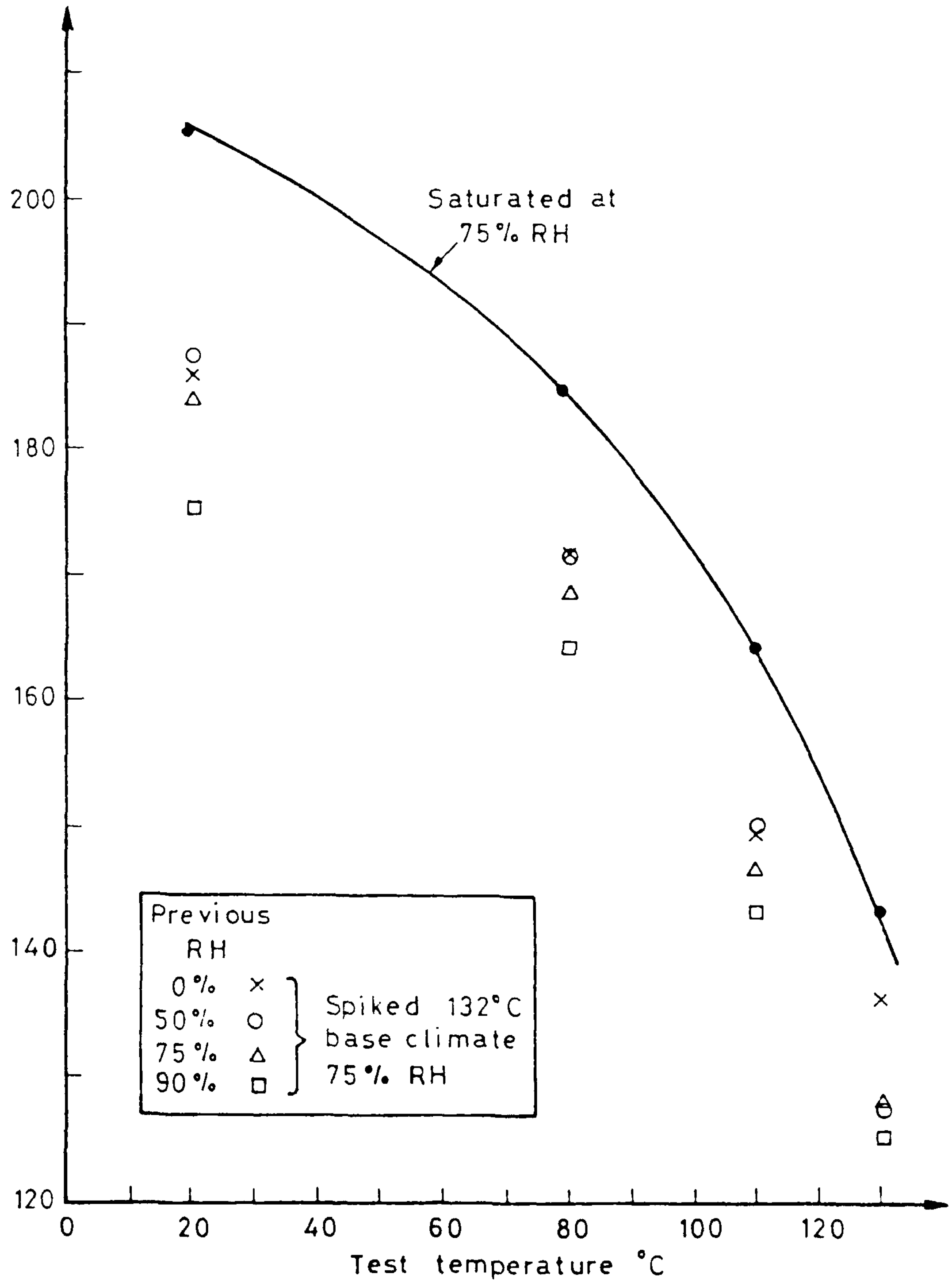
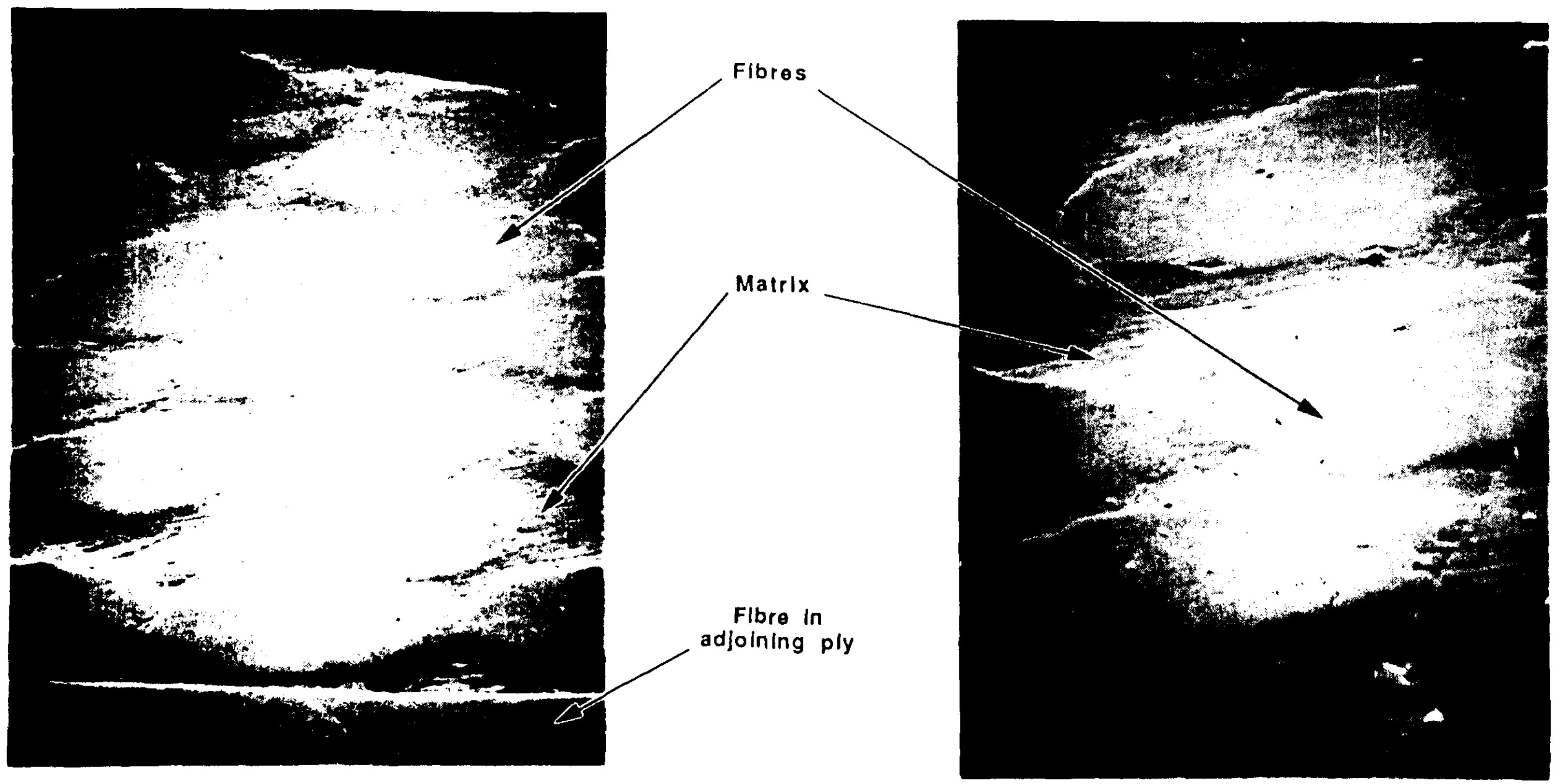


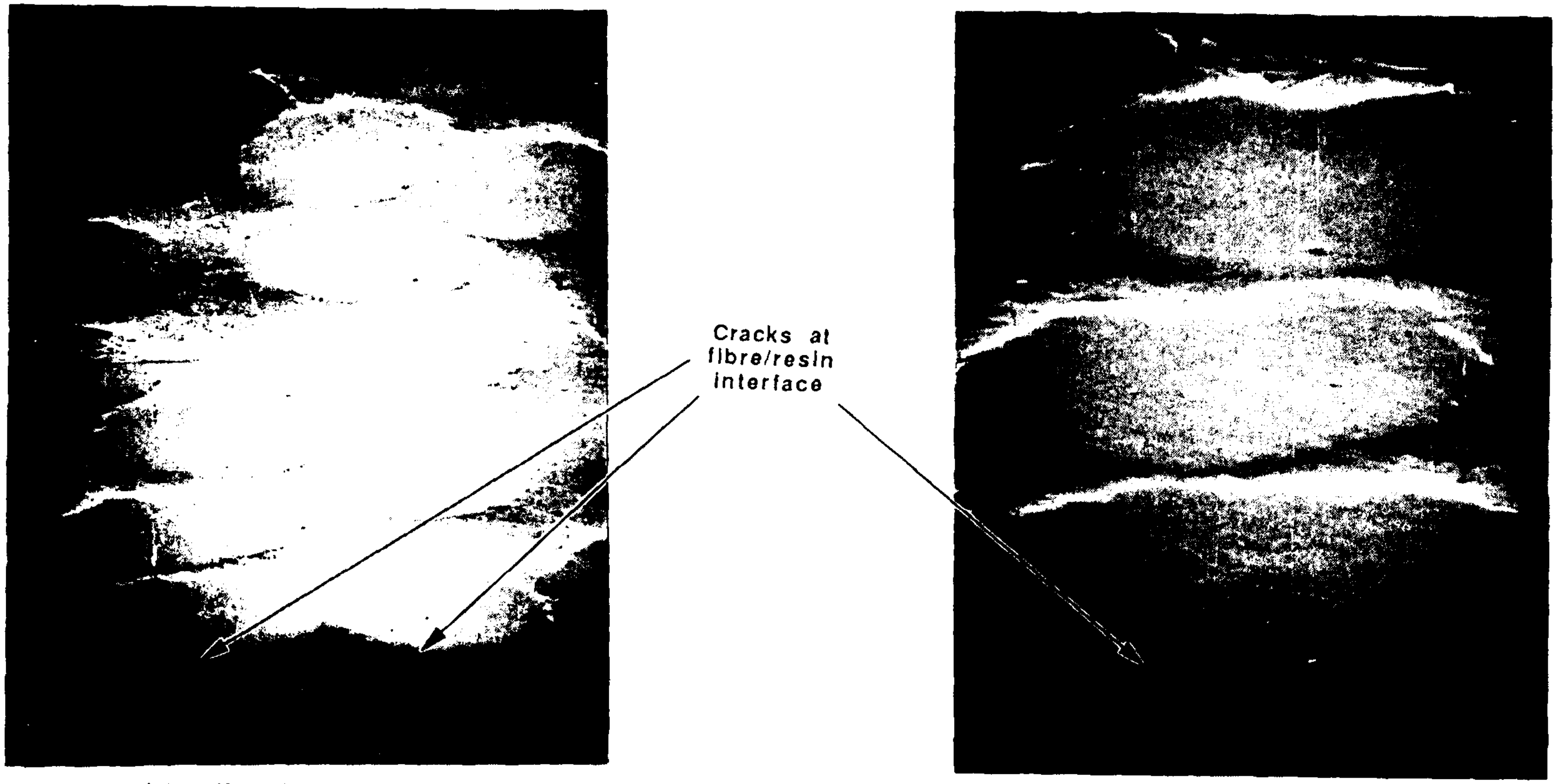
Figure 6 Failure stresses of the specimens described in figure 5.



(a) (X6,000)

(b) (X10,000)

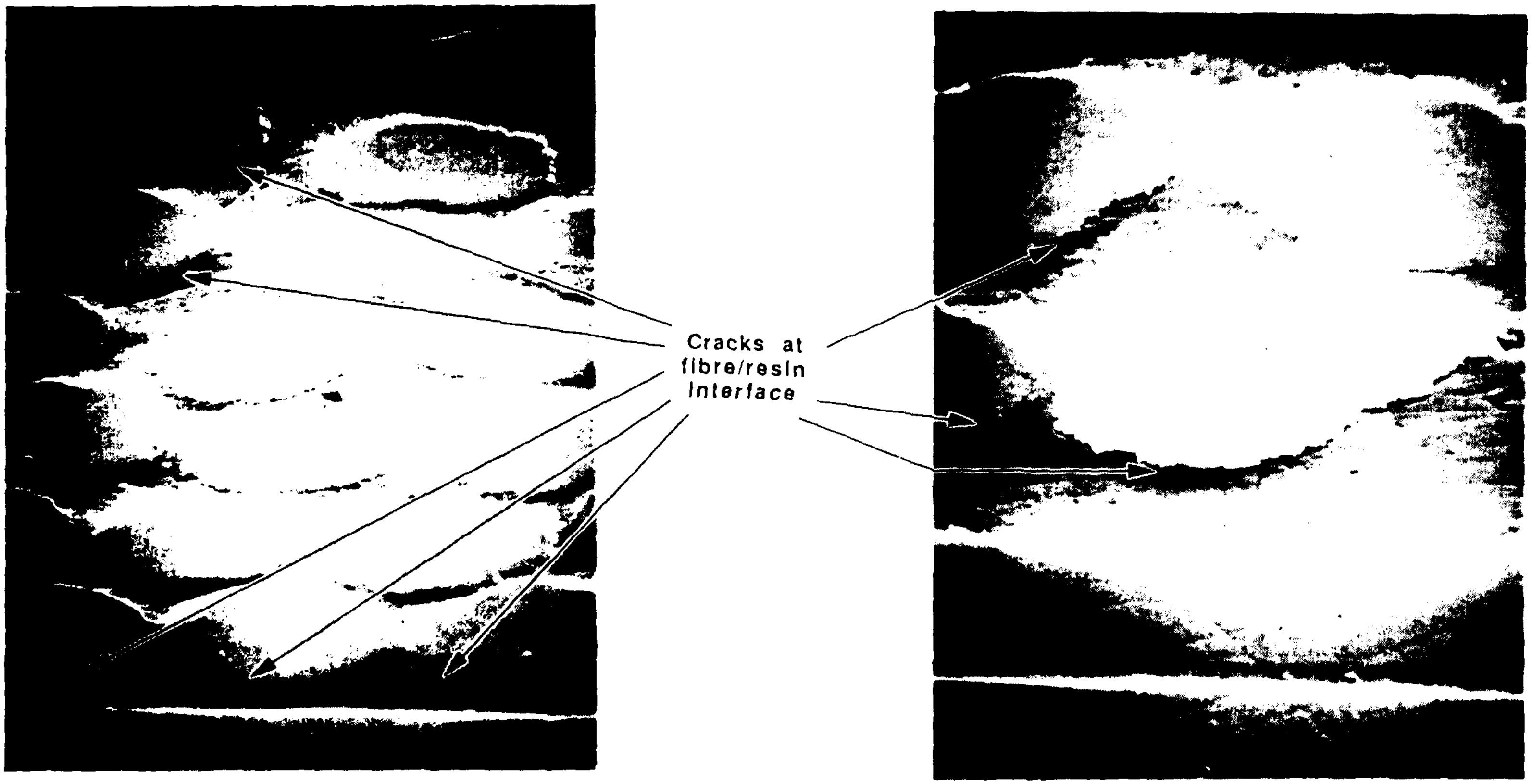
Figure 7 Micrographs of "as received" material.



(a) (X5,000)

(b) (X10,000)

Figure 8 Micrographs of non-spiked control conditioned in 60°C 90% RH environment.



(a) (X5,000)

(b) (X10,000)

Figure 9 Micrographs of real-life spiked specimen (-55/+132°C) with a base climate of 60°C 90% RH.